SULFUR HEXAFLUORIDE: A NOVEL FIXED POINT FOR CONTACT THERMOMETRY

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Abstract: In this paper, we report on the development at NRC of an immersion sulfur hexafluoride (SF_6) fixed point cell for calibrating long-stem standard platinum resistance thermometers. Discussed in detail are the unique challenges of constructing the high-pressure fixed point cell and realizing the triple point of SF_6 in a commercial stirred liquid bath.

1. INTRODUCTION

Recently, at the National Research Council of Canada (NRC) a cryogenic fixed point cell was filled with high purity (99.999 %) sulfur hexafluoride and measured in an adiabatic closed-cycle cryostat system using a capsule-type standard platinum resistance thermometer [1]. Based on this measurement, the temperature of the triple point of sulfur hexafluoride (TP SF_6) was shown to be 223.555 23(49) K (k = 1) on the ITS-90 - a value which agrees with the prior measurements reported in the literature and which has a considerably smaller uncertainty.

With the work of Rourke [1] providing a framework for the study, we set out to develop a sulfur hexafluoride triple point apparatus for calibrating long-stem standard platinum resistance thermometers (SPRT), an apparatus which would be relatively easy to construct and also simple to operate.

2. EXPERIMENTAL DETAILS

For our experiments, we opted to use a large metal immersion cell that can be directly dropped into a commercially available stirred liquid bath to realize the triple point of sulfur hexafluoride. Two immersion cells, one made out of copper (Cu) and one made out of stainless steel (SS), were manufactured and pressure certified for use up to 2.4 MPa by All Weld company (Canada). The Cu cell is made of regular copper, has three thermo-wells and an available volume for SF_6 of 990 cm^3. The SS cell is made of 304 stainless steel, has one thermo-well and an available volume of 420 cm^3.

Commercial sulfur hexafluoride from Concorde Specialty Gases, Inc. 99.999 % pure, containing only traces of water, air, CF_4 and carbon dioxide, was used to fill the cells without any additional purification steps. Prior to filling, each cell was degreased with organic solvents, pumped and flushed with SF_6 gas multiple times to dilute any gaseous impurities still remaining in the cell below 1 ppm level. Originally, we put approximately 830 g (360 g) of SF_6 in the Cu (SS) cell. Such an amount gives a filling ratio of 0.43 and the liquid depth of 10 cm at the triple point of sulfur hexafluoride. We have also tried a filling ratio of 0.79 for stainless steel cell.

SF_6 slow melting plateaus were recorded using an AC resistance bridge and an quartz sheath SPRT calibrated in NRC's contact thermometry comparison facility (1 mK uncertainty). During some of the melts, we tried initiating the inner melt after the melting plateau was reached by inserting for a different amount of time a metal rod at room temperature or a 7.5 W immersion heater in the thermal well.

3. RESULTS AND DISCUSSION

3.1. Results for Cu immersion cell

Chronologically, the Cu cell was made first. Copper was chosen for its high thermal conductivity and the ability to smoothen any temperature fluctuations present in the stirred liquid bath. Contrary to our expectations, it was discovered in the course of experiments that the temperature fluctuations in the bath were actually transmitted to the thermometer instead of being dampened: when the bath temperature control failed during an SF_6 freeze and the coolant pressure was oscillating ±10 psig, so did the temperature measured by SPRT in a thermal well of the copper cell. We speculated that the combination of high thermal conductivity and large mass of copper together with the low thermal conductivity of SF_6 are responsible for the observed behavior.

3.2. Results for SS immersion cell

The SS cell is less affected by small temperature fluctuation in the environment due to lower thermal conductivity and higher specific heat capacity of stainless steel compared to copper. For most of our experiments, we used commercially available Fluke 7080 stirred liquid bath (Bath 1) filled with ethanol (38 cm liquid depth). The sufficient immersion of the cell was verified in the custom made Hart Scientific 7081 (Bath 2) stirred liquid bath (46 cm liquid depth).

In all the cases, we were unable to obtain a flat long-lasting plateau with temperature stability within 0.1 mK. Without an inner melt initiation, the temperature would steadily rise, eventually passing the adiabatic cell result. However, it would not reach the bath setting even after 13 - 14 h of the experiment. With an inner melt initiation, there were two distinct regimes present: first regime (in the beginning of the melt) - with less temperature fluctuations and a relatively flat melting plateau, and second regime (later during the melt) - with a large number of temperature fluctuations present (sometimes spanning 10 – 15 mK).

Slow steady temperature rise in the experiments without an inner melt initiation is not surprising considering the low thermal conductivity of SF_6. Combined with unpredictable temperature fluctuation in the bath, it leads to the dynamic measurement error which renders any temperature measurement practically meaningless. To isolate the immersion cell from its environment, we designed a vacuum jacket that can fit both SS and Cu cells and can be placed into the rectangular opening of the Fluke 7080 stirred liquid bath.

Furthermore, temperature fluctuations observed in the experiments with an inner melt initiation might be indicative of insufficient immersion of the thermometer in SF_6. In order to check whether this is the case, we have performed additional experiments with twice the amount of SF_6 in the SS. The resulting melting plateaus obtained with the cell directly immersed in the bath or with the cell in a vacuum jacket are shown in Figure 1.

There is a substantial downward shift of 30 mK for the SS cell (0.79 filling ratio) in the vacuum jacket compared to the adiabatic cell result. This shift is repeatable when different amount of heating is provided by an immersion heater. There is a somewhat smaller downward shift of 5 mK when the

SS cell immersed directly in the bath. Overall, the plateaus' quality had much improved and the plateaus were lengthened.
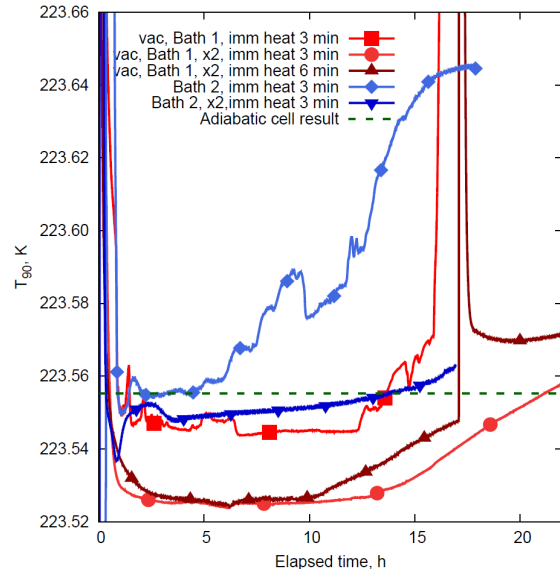
Fig. 1. *Comparison of the slow melts of SF_6 in the stainless steel immersion cell with 0.43 and 0.79 (x2) filling ratio immersed directly in a bath (Bath 2) or encased in a vacuum jacket (vac, Bath 1). Immersion heater was used for an indicated amount of time to initiate the inner melt.*

The reason for the downward temperature shift of the melting plateaus measured in the SS cell with and without the vacuum jacket after adding extra sulfur hexafluoride is currently unknown. To verify a few possible explanations - contamination of SF_6 in the cell, uncontrolled heat leaks to the environment and non-equilibrium thermodynamics of the phase transition - will be the subject of our future work.

5. CONCLUSIONS

We have described the current progress in developing a simple sulfur hexafluoride triple point apparatus at NRC. The best SF_6 melting plateaus we were able to obtain so far in terms of duration and temperature stability were measured with the stainless steel metal immersion cell encased in the vacuum jacket

REFERENCES

[1]   P. M. C. Rourke, "The triple point of sulfur hexafluoride", Metrologia, vol. 53, pp. L1-L6, 2016.